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<p>(21) International Application Number: PCT/US96/14098 (22) International Filing Date: 3 September 1996 (03.09.96) (30) Priority Data: 08/522,815 1 September 1995 (01.09.95) US (71)(72) Applicant and Inventor: BLUM, Ronald, D. [US/US]; 5320 Silver Fox Road, Roanoke, VA 24014 (US). (74) Agents: WELLS, William, K., Jr. et al.; Kenyon &amp; Kenyon, 1025 Connecticut Avenue, N.W., Washington, DC 20036 (US).</p>		<p>(81) Designated States: AL, AU, BB, BG, BR, CA, CN, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>
<p>(54) Title: METHOD AND COMPOSITION FOR THE MANUFACTURE OF OPHTHALMIC LENSES</p> <p>(57) Abstract</p> <p>A curing method for ophthalmic lenses or semi-finished lens blanks wherein a curable resin is first exposed to radiation in the wavelength range of 400-800 nm and subsequently subjected to heat or radiation of different wavelength or intensity than that used in the first step. The polymerizable resin preferably comprises: (1) a first photoinitiator that is activated by radiation in the wavelength range of 400-800 nm and (2) a thermal initiator which is activated by heat, or a second photoinitiator which is activated by radiation of different wavelength or intensity than that used to activate the first photoinitiator.</p>		

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METHOD AND COMPOSITION FOR THE MANUFACTURE  
OF OPHTHALMIC LENSES

FIELD OF THE INVENTION:

This invention relates to improved methods by which plastic resins can be cured to form ophthalmic lenses, semifinished blanks and optical preforms. Ophthalmic  
5 lenses often have complex geometries, with certain prescriptions having variations in thicknesses across the optic area of greater than an order of magnitude. Since the curing process is accompanied by shrinkage, a key objective of curing process development efforts is  
10 to be able to accommodate shrinkage without unduly increasing the cure time. I have developed a curing method for ophthalmic lenses that uses visible light to initiate cure, while nevertheless creating a colorless product.

15

BACKGROUND:

Curing of organic polymerizable resins to form ophthalmic lenses and semifinished blanks has traditionally involved the use of thermal polymerization  
20 initiators as described, for example, in US Patent

3,038,210, issued to Hungerford, et al., and US Patent 3,222,432, issued to Grandparret. More recently, photocuring processes have been disclosed involving the use of ultraviolet initiators, for example, US Patent 5 4,166,088, issued to Neefe, and US Patent Nos. 5,364,256 and 4,879,318 to Lipscomb. Photocuring processes have allowed the development of cure cycles that are considerably shorter than standard thermal curing cycles.

10 In all cases, it is necessary to ensure that the cure profile, which determines the rate of shrinkage, allows the cure of the bulk resin to take place in a controlled fashion while the surface still retains substantial adhesion to the mold. In this way, the lens 15 does not undergo a prerelease, does not develop optical aberrations caused by the formation of local heterogeneities in the resin mass due to uneven flow, and does not develop surface defects or cracks due to resin shrinkage.

20 In U.S. Patent No. 4,919,850, issued to me, I disclose a two stage cure process involving the use of ultraviolet polymerization initiators that allow the resin to gel under a low level of ultraviolet illumination. In this way, the initial cure rate is 25 maintained at a low level, until the resin mass becomes a gel and mass flow ceases within the curing lens. This is important, because the risk of developing optical aberrations is highest at the initial stages of the curing process when local exotherms can induce optical 30 aberrations through resin flow. After the material has undergone gelation, the cure rate is accelerated by increasing ultraviolet light intensity. Increasing light intensity also serves to maintain the pace of curing as the initiator becomes depleted. 35 Alternatively, the cure rate is also accelerated in the second stage by using UV light of a shorter wavelength.

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skill in the art upon reading the description and claims set forth below.

Unless indicated to the contrary, each reference cited herein is incorporated by reference in its  
5 entirety.

DETAILED DESCRIPTION OF THE INVENTION:

I have developed a cure process that utilizes room light in a first stage to initiate cure and reach the  
10 gel state. A second stage of the cure process can subsequently be completed, by application of thermal energy, by application of UV light, or both. The initial curing stage may take place either directly under room light, or in chambers employing visible light  
15 bulbs.

Since polymerization initiators which are activated by visible light are generally highly colored, it may appear at first sight that their use would be incompatible with the proposed application (i.e., to  
20 make an ophthalmic lens which is preferably colorless, or water white). Recently, a new class of photopolymerization initiators has been commercialized which begin as a colored species and are activated by visible light, but upon activation form colorless  
25 photodissociation products. I discovered that such photoinitiators can be used to develop cure processes for ophthalmic lenses and semi-finished blanks.

A preferred photoinitiator is BAPO, available from Ciba Geigy Corp. This photopolymerization initiator is  
30 actually a mixture of two photoinitiators, Bisdimethoxybenzoyl Trimethylpentyl Phosphine Oxide (25%, by weight) and 2-Hydroxy 2-Methyl 1-Phenyl Propanone (75% by weight). The phosphine oxide derivative absorbs visible light in the wavelength range  
35 400-450 NM range, and initiates polymerization of resins incorporating acrylic, methacrylic, vinylic or allylic derivatives.

Under normal room illumination, the cure rate is slow. Therefore, the mold assemblies do not require cooling or other temperature control to undergo gelation. Nevertheless, precise temperature control does produce a more uniform product and improves product consistency and yield. If temperature control mechanisms are provided, they should be employed to control the temperature at or near room temperature, i.e., at about 15°C to 35°C.

While not wishing to be bound by any particular theory, it is believed that this photoinitiator works in the following fashion. The phosphine oxide derivative is activated and undergoes photodissociation under room light, leaving the acetophenone derivative unaffected. The phosphine oxide derivative undergoes bleaching on photodissociation, so that the polymerizing resin mass becomes less colored as polymerization progresses. Once the resin has undergone gelation, the mold assembly is placed in a chamber equipped with ultraviolet light bulbs emitting radiation in the wavelength range of 300-380 NM. The near ultraviolet radiation activates the acetophenone derivative, causing the curing process to become accelerated. At the same time, the dissociation of the phosphine oxide derivative is completed, completing the bleaching process. A residual faint yellow hue can be corrected by an addition of a small amount of a bluing additive, such as TINOPAL (available from Ciba Geigy Corp.) to the resin formulation.

When UV photoinitiators (such as the acetophenone derivative) are used during the second stage of cure, the mold assembly may be heated along a preestablished temperature profile, ultimately reaching a final temperature in the range of about 90°-150°C, to complete the cure process and to obtain a final lens product with a glass transition temperature in the range of about 100°-175°C. If no heat is applied and the temperature maintained at or near room temperature, the final

product has a lower glass transition temperature (e.g., in the range of about 30°-50°C). In all cases, the cure process should be completed. The extent of the cure process can be monitored, for example, by a differential scanning calorimetric analysis of the material after  
5 cure. Whether heating is necessary to complete the cure generally depends on the monomers used in the resin formulation. Thus, if monomers used in the formulation can form homopolymers which have glass transition  
10 temperatures considerably above the room temperature (15°-30°C), then an elevated temperature is desirable to complete the cure process.

Alternatively, a phosphine oxide derivative may be used which initiates cure under visible light as before.  
15 However, a thermal polymerization initiator, such as a peroxide, a peracetate, a percarbonate or an azo derivative may be used to complete the second stage (post-gel cure) by placing the mold assembly in a thermal curing oven, typically a convection oven.

20 The two stage polymerization process described above may be carried out in glass molds, in metal molds or in a combination thereof. Metal molds with reflective inner surfaces may be especially useful in reflecting radiation back into the resin mass and  
25 conducting excess heat away from the resin mass. Metal molds may also be made thinner, and thus can have a lower thermal mass than glass molds. Alternatively, glass molds with metallized surfaces may be employed for resin formulations which require a metal mold for  
30 adhesion and thus prevent prerelease during cure.

The two stage polymerization method can be employed to produce lenses from resin formulations covering a wide range of chemical reactivities, functionalities, shrinkage properties, and thermal expansion  
35 characteristics. Both monomers and oligomers may be employed, and polymeric or small molecular weight additives can be included to alter physical properties



of the resin formulation, such as viscosity and surface energy, as well as chemical properties of the formulation, such as oxidative and photothermal or hydrolytic stability.

CLAIMS

What is claimed is:

- 1 1. A curing method for ophthalmic lenses or semi-  
2 finished lens blanks comprising:
  - 3 (A) providing a mold and a polymerizable resin, said  
4 polymerizable resin comprising
    - 5 (1) a first photoinitiator that is activated by  
6 radiation in the wavelength range 400-800 NM  
7 and
    - 8 (2) an initiator selected from the group consisting  
9 of (a) a thermal initiator which is activated  
10 by heat and (b) a second photoinitiator which  
11 is activated by radiation of different  
12 wavelength or intensity than that used to  
13 activate the first photoinitiator;
  - 14 (B) exposing the curable resin to radiation in the  
15 wavelength range of 400-800 NM; and
  - 16 (C) subsequently subjecting the curable resin to a  
17 curing environment selected from (1) heat and (2)  
18 radiation of different wavelength or intensity than  
19 that used in step (B).
- 1 2. The method of claim 1, further comprising heat  
2 treating subsequent to step (C).
- 1 3. The method of claim 1, in which light delivered by  
2 incandescent light bulbs is used to provide said  
3 radiation in the wavelength range of 400-800 NM.
- 1 4. The method of claim 1, in which light delivered by  
2 fluorescent light bulbs is used to provide said  
3 radiation in the wavelength range of 400-800 NM.
- 1 5. The method of claim 1, in which step (B) further  
2 comprises control of temperature in the range 15°C-45°C.

- 1 6. The method of claim 1, in which said first  
2 photoinitiator is Bisdimethoxybenzoyl Trimethylpentyl  
3 Phosphine Oxide.
- 1 7. The method of claim 1, in which said second  
2 photoinitiator is selected as the initiator.
- 1 8. The method of claim 7, in which said second  
2 photoinitiator is .2-Hydroxy 2-Methyl 1-Phenyl Propane.
- 1 9. The method of claim 1, in which said thermal  
2 initiator is selected as the initiator.
- 1 10. The method of claim 11, in which said thermal  
2 initiator is selected from the group consisting of a  
3 peroxide, a peracetate, a percarbonate and an azo  
4 derivative.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/14098

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B29D 11/00

US CL :264/1.36, 1.38, 1.7, 1.8

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 264/1.36, 1.38, 1.7, 1.8

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category <sup>a</sup>	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,919,850 A (BLUM ET AL) 24 April 1990, see whole document	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

<sup>a</sup>

Special categories of cited documents:

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document defining the general state of the art which is not considered to be of particular relevance

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